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(54) FOOD GELLING COMPOSITION

(71) We, CECA S.A., a French body corporate having its Head Office at 11, Avenue Morane Saulnier 78.140 Velizy-Villacoublay, France, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a gelling composition for use as a food gelling agent for water and milk.

According to the present invention, there is provided a gelling composition for use as a food gelling agent for water or milk, and comprising a gelling mixture constituted by a first gelling agent which is a galactomannan and a second gelling agent which is an agar and/or a xanthane, the galactomannan having undergone a depolymerisation treatment such that its 1% by weight solution in water has a viscosity in the range of 10 to 1000 centipoises at 25°C measured using a Brookfield R.V.T. viscometer at 20 r.p.m.

The invention also provides gelled water and more particularly milk based products in which gelling is achieved by means of this gelling composition. Also of interest are fruit juice based gel products in which gelling is achieved by means of this gelling composition. The gelling composition is a particularly useful component of water or milk based gels of an acidic nature.

The gelling agents normally used to gel milk are sulphated polysaccharides: carraghenans, furcellarans and agars. The products give good results with a milk whose pH is close to 6. When such gelling agents are used with acidified milk whose pH is often close to 4, floculation of the casein occurs thereby rendering the appearance and quality of the product unsatisfactory and giving the product a texture such that it is unpleasant to eat. This phenomenon is particularly noteworthy with sulphated polysaccharides as against other gelling agents since they precipitate with the caseic under such pH conditions.

Research has therefore been carried out to find what improvements can be made in these gelling agents, particularly agar.

The addition of a galactomannan, such as locust bean gum, to agar appears to result in avoidance of the precipitation of the casein. However the gels obtained are stiff and do not have the organoleptic qualities currently designated by the term "mouth feel"; if the quantity of galactomannan, such as locust bean gum which is used increases to a value which is larger than that of agar, the problem of unsatisfactory "mouth feel" is largely overcome. However, the cohesiveness of the gel is still high and the gel has a disagreeable rubbery texture.

The applicants have now found, that a gel of very agreeable consistency and having none of these disadvantages can be obtained by using a depolymerised galactomannan, i.e. a galactomannan having a degree of polymerisation reduced by physical, chemical or biochemical means. An easy method of achieving this depolymerisation is by subjecting galactomannan to the action in solution of hydrogen peroxide or of an acid. More precisely, the requisite polymerisation degree is such that a 1% by weight solution of the galactomannan in water has a viscosity in the range of 10 to 1000 preferably 300 to 1000 centipoises at 25°C as measured by a Brookfield R.V.T. viscometer at 20 r.p.m.

When subjected to measuring conditions, aqueous solutions of undepolymerised

galactomannans have a high viscosity; for example locust bean gum has a viscosity of 1200 to 3600 centipoises.

In addition, the mouth feel of the gel is again improved by using agar and the galactomannan in the form of a homogeneous mixture btained by coprecipitation by a solvent from a mixture of the agar extract and the galactomannan extract. Agar is normally obtained from solution thereof by cooling to achieve gelation followed by heating; it is difficult to obtain the coagulation of agar in solution in water using an organic solvent such as methyl alcohol, isopropyl alcohol or acetone. On the other hand, coagulation occurs perfectly well if one uses a mixture of solutions of agar and the depolymerised galactomannan. Alcohol should preferably be used as a solvent.

Such coagulation from mixed solutions works well because the agar is then coagulated by alcohol in the form of a complex in which the agar is homogeneously distributed. It has additionally been found that agar, may be replaced in part or in whole, in compositions of this invention by a polysaccharide of microbial origin, in particular, a xanthane and that moreover another polysaccharide, in particular a carraghenan, furcellaran or pectin may additionally be incorporated in the composition. In this case, nevertheless, one obtains slightly more heterogeneous structures.

The depolymerised galactomannan used in a gelling composition of this invention may be more particularly obtained from a locust bean, tar or Espina corona base. The ratio by weight between the second gelling agent and the depolymerised galactomannan is preferably from 1:1 to 1:9.

A gelling composition of this invention may be used as a food gelling agent in an aqueous medium, in particular but not exclusively, milk, either at a pH close to 7 or after acidification; this acidification may be achieved more particularly by adding a fruit juice. In the case of milk, this acidification may be obtained by microbioal action of the type which leads to formation of yogurt. In general, whether acidified water, acidified milk or fruit juice is employed, the concentration of the gelling composition therein is preferably from 0.1 to 4% by weight.

Yogurt is a product having a gel texture obtained by adding to milk, which is generally pasteurised, cultures of certain bacterial strains which acidify the milk through a coagulation of the casein. The transformation of milk to yogurt is effected at a temperature close to 40°C.

If the yogurt is preserved at ambient temperature, the bacterial strains continue their action, the acidity continues to develop, the product loses its qualities and its shelf life is thereby limited.

This shelf life is appreciably improved if the bacterial strains are killed by heat; as this operation usually m difies the texture f the product, it is advisable to add a gelling agent to palliate this disadvantage; this addition is usually made to milk before pasteurisation or to yogurt after fermentation.

This heating, currently called thermization, is nevertheless limited to temperatures of approximately 70°C with common gels. Above this temperature, the protecting effect of the gel reduces gradually and the casein undergoes a dehydration process leading to a heterogeneous texture which is characteristically "sandy" and very disagreeable, possibly leading to total separation if the temperature rises too much.

It has in fact been found that when use is made of the gelling composition of this invention, yogurt can be treated at very much higher temperatures without the product's losing its homogeneity. This thermization at a higher temperature, i.e. higher than 70°C allows the product obtained to have a longer preservation shelf life by ensuring that better destruction of the bacterial strains occurs.

Thermization can be carried out on the product either directly which is most sterile way possible, or on the product after it has been placed in containers and hermetically sealed therein.

The product may be yogurt by itself or yogurt mixed with other dairy products, for example fresh cheese or cottage cheese or non-dairy products, for example fruit, jams, preserved fruit, vegetables, seasoning herbs and spices, as well as with sugar, salt, flavourings, colourings, etc.

The invention will be better understood by means of the following examples in which gelling agents prepared according to the following methods have been used. All viscosity measurements in the following preparative methods and specific examples were measured using a Brookfield R.V.T. viscometers at 20 r.p.m.

Preparative Method I

PREPARATION OF A DEPOLYMERISED LOCUST BEAN EXTRACT:

30 kg of locust bean meal were introduced with stirring into 2 m^3 of water at 80°C. Once the gum had been well solubilised the solution was heated to 90°C and 0.6 litre of hydrogen peroxide at 110 volumes was added thereto.

The viscosity of the solution was measured at regular intervals. After 4 hours, the viscosity was 200 centipoises. A concentration check indicated the solution contained about 1% by weight of soluble locust bean gum. The solution was then filtered through a press filter using 13 kg/m^3 of a filtering aid. The clear solution thus obtained was cooled to 40°C.

Instead of using the 30 kg of locust bean meal it would have been possible to have used 33 kg of locust bean splits and obtained the

TABLE 1

Viscosity of solution containing locust bean extract in 1% by wt. concentrati n in form of complex (Centripoises)	Gel Stiffness (Grams)	Gel Cohesiveness (Grams)
60	58	120
150	64	350
360	69	620
900	68	900
1170	69	2100
2000	69	2500
3000	70	2400

same results.

Preparative Method II

The procedure of Preparative Method I was repeated but using sulphuric acid until the pH of the gum solution reached 4. At the end of 5 hours, the viscosity of the solution had dropped to about 200 centipoises. Degradation was then stopped by neutralization and the solution obtained was then worked up in the manner set out in Preparative Method I.

Preparative Method III

PREPARATION OF AN AGAR EXTRACT:

A solution of an agar extract was prepared by washing 35 kg of seaweed (Gracilaria, Gelidium or Pterocladia) by immersion in 500 litres of water for 2 hours. The seaweed was then heated under pressure at 1100°C for 6 hours in 1 m^3 of water. The aqueous medium was then separated from the seaweed by filtration through a press filter using 12 g/l of a filtering agent. The filtrate thereby obtained contained agar in a concentration of about 1% by weight.

Preparative Method IV

COAGULATION BY ALCOHOL OF MIXTURE OF SOLUTIONS OF GALACTOMANNANS AND AGAR:

The solutions of the depolymerised locust bean extract i.e. depolymerised galactomannan and agar obtained in Preparative Methods I and III respectively were mixed in the required proportions. For example, 1 volume of agar solution of 1% by weight concentration and 3 volumes of depolymerised locust bean solution at 1% by weight concentration, were combined and brought to a temperature of 50°C and then poured into 7 volumes of isopropyl alcohol (azeotrope), the depolymerised agar-locust bean gum complex separated out in the form of fibres which were pressed, washed, dried and crushed.

Alternatively the 4 volumes of mixed solution could have been coagulated using 6 volumes of methanol and acetone.

EXAMPLE 1

To study the effect of the organoleptic properties of locust bean gum of the depolymerisation thereof, solutions of locust bean gun depolymerised to different extents as described in Preparative Method I were coagulated with an agar solution to obtain a final mixture containing 25% by weight of agar and 75% by weight of locust bean gum. The depolymerisation of the locust bean gum was measured by taking a sample of its solution as prepared above and coagulating it; after drying, the viscosity at 1% by weight concentration of this locust bean extract was measured. The complexes of agar and locust bean gum obtained were used at 1% by weight concentration to make aqueous gels by dissolution on boiling and cooling of the solution.

The characteristics of the gels obtained were measured in two ways:

a: the gell stiffness was measured by determining the force required to sink a 1.1 cm diameter piston to a depth of 4 mm into the gel;

b: the gel cohesiveness was measured by determining the force required to crush a body of gel 6 cm in diameter and 4 cm high with a 10 cm diameter plate, the gel not being constrained laterally in any way, Table 1.

This acid phase is added to the neutral solution containing the gelling agent and kept at a temperature between 50°C and 80°C while subject to stirring or any other form of mixing operation to prevent the pH of the mixture from falling locally below 4.

The product is then heat-conditioned. It gels during cooling. The product may also be cooled below its gelling temperature before conditioning. This cooling may be carried ut by stirring, either in a vat or by passing through a heat-exchanger, and a non-gelled product of the dessert-cream or liégois type is then obtained.

EXAMPLE 2

ACIDIFICATION BY ADDING A FOOD ACID

Basic formula (all percentages expressed on a weight basis)

Neutral phase	
milk having a 1.5% by weight fat content	81.56%
sugar	16%
fruit flavouring	1%
fruit colouring	0.04%
agar-depolymerised locust bean gum complex as gelling agent	0.6%
Acid phase	
citric acid	0.8%
	(in solution at 50%)
Final pH	4.3 to 4.5

The gelling agent, previously mixed with sugar, was dispersed in the milk. The mixture was heated to 80°C and then sterilised by passing through a UHT steriliser where it was subjected to steam injection at 147°C for 3 seconds before being cooled at 60 to 70°C., at which temperature the acid phase was added.

In order that the sugar, fruit flavouring and fruit colouring should not be subject to degradation during the high-temperature treatment, this is included in the acid phase.

The product obtained on adding the acid phase was then cooled. An acid milk gel having a very smooth and melting temperature and which could be easily removed from a mould was obtained.

EXAMPLE 3

The procedure of Example 2 was repeated, but with the difference that cooling was effected by passing the solution through a scraped-surface type of heat-exchanger at 10°C. A milk cream having a smooth and oily texture was obtained.

EXAMPLE 4

ACIDIFICATION BY ADDING A CONCENTRATED FRUIT JUICE

Basic formula (percentages expressed on a weight basis):

Neutral phase	
milk having a 1.5% by weight fat content	78.38%
sugar	16%
fruit colouring	0.02%
agar-depolymerised locust bean gum complex	0.6%
Acid phase	
concentrated fruit juice	5%

Operational method: the same as Example 2.

The accompanying drawing is a graph showing gel stiffness and gell cohesiveness plotted against solution viscosity.

These results show that in an agar-locust bean gum gel:

– the gel stiffness varies little with the extent to which depolymerisation of the locust bean gum used has occured;

– the gel cohesiveness varies with the extent to which depolymerisation of the locust bean gum has occurred.

In addition, tests which have been carried out show that for different proportions of agar and locust bean gum,

– locust bean gums having viscosities higher than 1000 centipoises give a product gelled therewith very great cohesiveness so that on tasting, the product tends to have a rubbery consistency;

– the locust bean gums having viscosities in the range of 300 to 800 centipoises have less cohesiveness and a greater tendency to "melt in the mouth";

– locust bean gums having a viscosity lower than 300 centipoises exhibit the tendency to "melt" to an even greater extent, but the gels become difficult to remove from moulds.

EXAMPLES OF ACID MILK GELS:

The stability of a depolymerised agar-locust bean gum complex in an acid medium makes it a particularly valuable product to use in acid milk gels. In addition use of the complex avoids casein precipitation when operating below the isoelectric point of the milk (more particularly of the casein).

Moreover the agar and depolymerised locust bean gum, being practically neutral, do not undergo coprecipitation with the milk casein, as opposed to the carraghenans or the furcelleran which are the usual dairy gelling agents, at least in a neutral medium and, in addition, serve to prevent casein precipitation by encasing the colloidal particles of casein.

Two stages are involved in the commercial production of acid milk gels:

FIRST STAGE: PREPARATION OF A NEUTRAL SOLUTION CONTAINING A GELLING AGENT

The gelling agent, sugar and other ingredients, except the acid, are dispersed in fresh or reconstituted milk. The mixture is then heated to place the various ingredients in solution and to sterilise the product partially or totally. This treatment may be a standard pasteurisation treatment in a vat or in heat-exchangers, sterilisation by steam injection (UHT) or any other very high temperature treatment using a heat-exchanger or friction. The temperatures used vary from 80 to 150°C. The mixture is then cooled to

between 50 and 80°C., so as to be at a temperature higher than the gelling temperature.

SECOND STAGE: ADDITION OF THE ACID PHASE

The acid phase may be constituted by

A) a food acid in solution;

B) a fruit juice, which may be concentrated and which may contain fruit pulp; or

C) a dairy product acidified for example by fermentation, as with yogurt.

EXAMPLE 5

The operational method of Example 3 was repeated using the composition of Example 4.

EXAMPLE 6

ACIDIFICATION BY ADDING AN ACID DAIRY PRODUCT

Basic formula	
milk having a 1.5% by weight fat content	20%
sugar	5%
agar-depolymerised locust bean gum complex	0.6%
Acid phase	
yogurt	74.4%

Operational method: the same as Example 2 except that the acid phase was raised to 40 to 45°C before addition to the neutral phase.

EXAMPLE 7

The procedure of Example 6 was repeated but cooling at the end of the experiment was effected by the method set out in Example 3.

The product thus obtained was similar to a mixed yogurt. Three other acid phase compositions were also used in combination. For example:

A + B: the flavouring was contributed by fruit juice or pulp but the acidity was strengthened by the addition of a food acid;

C + B: the flavouring was modified by the addition of pulp or fruit juice which was or was not concentrated;

C + A: the acidity was strengthened by the addition of a food acid.

Due to their acidity and the preparation technique, the products thus obtained had a longer shelf life than the neutral dairy products.

EXAMPLES OF WATER BASED GELS

The gelling agents such as the carraghenans and gelatine usually used to obtain, in an acid medium, an edible gel having a non-brittle texture, have the defect of depolymerising considerably when subject to the thermic treatments indispensable to their preparation. This depolymerisation is a function of the acidicity and makes these products unusable at pH lower than 3.6. The gelling agents of this invention behave better in acid media and enable elastic and oily gels to be obtained at relatively low pH. In the case of water-based fruit gels, these acidity conditions favour the development of the fruit flavours and the products btained are superior t those usually prepared with the carraghenans or gelatine. The good behaviour in an acid medium thus allows the use of fruit juices themselves as flavouring agents.

EXAMPLE 8

WATER-BASED GELS WITH FOOD ACID

To 500 ml of water, there were added the following, in powder form:

Sugar	85 grams
Strawberry flavouring	1.5 grams
Strawberry colouring	0.02 grams
Citric acid	1 gram
Agar-depolymerised locust bean gum complex	4 grams

The powders were first premixed and then added to boiling water. The solution obtained was returned to boiling point and poured into a container. A gel was obtained which was transparent, elastic and unctuous. The gel had a pH of 3.3.

EXAMPLE 9

FRUIT JUICE-BASED GELS

A premix of 15 grams of sugar and 1.2 grams of agar-depolymerised locust bean gum complex was first formed. This was then dispersed in 58.8 grams of water which was brought to boiling point before being cooled to 80 to 90°C when 25 grams of concentrated fruit juice were added. After standing, a fruit juice-based gel was produced. It is possible to use for this purpose a concentrated fruit juice with or without pulp.

EXAMPLES OF YOGURT

Polysaccharide-galactomannan mixtures which were used in the production of yogurts in the following examples were the following:

1) Deploymerised locust bean gum	70% by wt.
Agar	30% by wt.
2) Depolymerised locust bean gum	65% by wt.
Xanthane	35% by wt.
3) Depolymerised locust bean gum	55% by wt.
Pectin	45% by wt.
4) Depolymerised locust bean gum	75% by wt.
Agar	20% by wt.
Carraghenan	5% by wt.
5) Depolymerised locust bean gum	55% by wt.
Agar	10% by wt.
Pectin	35% by wt.

EXAMPLE 10

a) PREPARATION OF THE YOGURT

A yogurt was prepared in a standard manner. 3 kg of milk powder were added to 100 litres of milk; the milk was heated for several minutes at 90°C or sterilised by passing through a UHT steriliser, then homogenised. The enriched milk could also have been prepared by light concentration after thermic treatment of the initial milk on vacuum cooling.

The milk thus obtained was cooled to 40 to

45°C. The required ferment containing a mixture of bacterial strains was then added thereto and the milk was left until the desired acidity was obtained. The time period required for this purpose depended on the chosen ferments and temperatures.

The yogurt obtained was cooled to below 10°C to prolong its shelf life by inactivating the ferment. Alternatively, if a so-called live yogurt was to be obtained, such cooling was omitted.

b) ADDITION OF THE GELLING COMPOSITION

Formula of the product:

99.6% by weight yogurt,
0.4% by weight of a gelling composition according to the invention.

The gelling composition was added with vigorous stirring to the yogurt. The mixture was heated in a vat at 95°C and maintained at this temperature for a period ranging from several minutes to 1 hour. During all these heating operations, it was necessary to ensure that the difference in temperature between the product and the heating fluid was as small as possible.

c) The mixture was then homogenised and put into pots at high temperature to maintain the sterility. Gelification, giving the product its traditional yogurt look, took place during cooling of the mixture. If desired, the homogenisation step could have been omitted.

EXAMPLE 11

Stages a) and b) of Example 10 were repeated.

c) After heating the product of stage b) at 95°C., the product was subjected to heating to very high temperature in a heat-exchanger (of the plate, tubular or scraped-surface type). While ensuring that the difference in temperature between the product and the heating fluid was very small, the temperature of the product was thereby increased to 100 to 110°C.

After cooling to between 90 to 70°C, the product was homogenised. It was allowed to stand under sterile conditions so as to increase its shelf life.

EXAMPLE 12

Stages a) and b) of Example 10 were repeated.

c) The product of stage b) was allowed to stand in pots or metal boxes optionally after undergoing homogenisation. The containers were kept at temperatures of up to 110°C in static autoclaves for a length of time chosen in accordance with the desired sterility.

EXAMPLE 13

Stages a) and b) of Example 10 were repeated.

c) The product obtained was cooled to 60°C then mixed with other dairy products. In different tests fresh cheese and cottage cheese (fat or non-fat) were used in different proportions. One such formulation was as follows:

stabilised yogurt 50% by weight (49.2% by weight yogurt, 0.8% by weight gelling composition);
fresh cheese having a 2% by weight fat content: 50% by weight.

The mixture was then heated up to 100°C as in Example 11 by passing through heat-exchangers and was directly put into pots and heated as in Example 12 up to 100°C.

As an alternative to adding dairy products to stabilised yogurts produced according to this invention it is also possible to add to yogurt as to yogurt-fresh cheese mixture, one or more of the following ingredients: sugar, flavourings, colourings, fruit, jam, preserved fruit, salt, vegetables, spices and seasoning herbs.

EXAMPLE 14

The procedures of Examples 10 to 13 were repeated but using the following formulation:

yogurt	89.6% by wt.
gelling agent	0.4% by wt.
sugar	10% by wt.

The gelling agent was premixed with the sugar which facilitated its dispersal in the yogurt.

EXAMPLE 15

The procedures of Examples 10 to 12 were repeated using the following formulation:

yogurt	81.6% by wt.
sliced fruit	10% by wt.
gelling agent	0.4% by wt.
sugar	8% by wt.

The fruit was added at the stage when the yogurt was at 95°C.

EXAMPLE 16

The procedure of Example 13 was repeated using the following formulation:

yogurt	41.5% by wt.
fresh cheese having a 20% fat content	40% by wt.
preserved fruit	18% by wt.
gelling agent	0.5% by wt.

The preserved fruit was added at the same time as the fresh cheese.

EXAMPLE 17

The procedures of Examples 10 to 12 were repeated using the following formulation:

yogurt	84.5% by wt.
preserved fruit	15% by wt.
gelling agent	0.5% by wt.

The preserved fruit was added at the stage when the fruit was at 95°C.

EXAMPLE 18

The procedure of Example 13 was repeated using the following formulation:

yogurt	48.5% by wt.
fresh cheese having a 20% fat content	48.5% by wt.
dried seasoning herbs	0.5% to 1% by wt.
gelling agent	0.5% by wt.

salt 2% by wt.

The salt and the seasoning herbs were mixed with the gelling agent and dispersed in the yogurt. They could also have been added to the fresh cheese before addition thereof to the yogurt.

WHAT WE CLAIM IS:—

1. A gelling composition for use as a food gelling agent for water or milk, and comprising a gelling mixture constituted by a first gelling agent which is a galactomannan and a second gelling agent which is an agar and/or a xanthane, the galactomannan having undergone a depolymerisation treatment such that its 1% by weight solution in water has a viscosity in the range of 10 and 1000 centipoises at 25°C measured using a Brookfield R.V.T. viscometer at 20 r.p.m.

2. A gelling composition according to claim 1, wherein the galactomannan has a degree of polymerisation such that its solution at 1% by weight solution in water has a viscosity in the range of 300 and 1000 centipoises at 25°C measured using a Brookfield R.V.T. viscometer at 20 r.p.m.

3. A gelling composition according to claim 1 or 2, wherein the second gelling agent also comprises a polysaccharide which is a carraghenan, furcellaran or pectin.

4. A gelling composition according to any one of claims 1, 2 or 3, which is obtained by precipitation of the constituents of the first and second gelling agents, from a mixture of solutions thereof using an organic liquid.

5. A gelling composition according to any one of claims 1 to 4, wherein the galactomannan is a depolymerised extract of locust bean, tara or Espina corona.

6. A gelling composition according to any one of claims 1 t 4, wherein the galactomannan is the product of treating locust bean, tara or Espina corona meal to obtain depolymerisation of the gum content thereof.

7. A gelling composition according to any one of claims 1 t 6, wherein the weight ratio between the second gelling agent and the depolymerised galactomannan is from 1:1 to 1:9.

8. A gelling composition as claimed in claim 1, substantially as described herein.

9. A gelled product which is a water, milk or fruit juice-based product containing a gelling composition as claimed in any one of the preceding claims.

10. A gelled product as claimed in claim 9, which is an acidified water or milk-based product.

11. A gelled product, as claimed in claim 10, wherein the acidified milk-based product is a yogurt.

12. A gelled product as claimed in claim 11, wherein the yogurt has undergone a thermic treatment at a temperature higher than 70°C.

13. A gelled product, as claimed in any one of claims 9 to 12, wherein the gelling composition is present in a concentration of from 0.1 to 4%.

14. A gelled product as claimed in claim 9, substantially as described in any one of the foregoing Examples 2 to 18.

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1565006 COMPLETE SPECIFICATION

1 SHEET *This drawing is a reproduction of the Original on a reduced scale*